

PUBLICATION NUMBER : 08040737  
PUBLICATION DATE : 13-02-96

APPLICATION DATE : 03-08-94  
APPLICATION NUMBER : 06182353

APPLICANT : SHIN ETSU CHEM CO LTD;

INVENTOR : SUZUKI MASAYUKI;

INT.CL. : C03B 20/00 C01B 33/18 C03B 8/02 C03C 3/06

TITLE : HIGH-VISCOSITY SYNTHETIC QUARTZ GLASS MEMBER AND ITS PRODUCTION

ABSTRACT : PURPOSE: To obtain a high-viscosity synthetic quartz glass member, containing uniformly distributed Al and having a high-temperature viscosity above that of an electrofused natural quartz glass according to a sol-gel method.

CONSTITUTION: This method for producing a high-viscosity synthetic quartz glass member is to add an aluminum alkoxide to methyl silicate, cohydrolyze the resultant mixture in the presence of ammonia, prepare silica particles containing aluminum, dehydrate, decarbonize and sinter the silica particles, afford a synthetic quartz glass ingot, pulverize the resultant ingot and melt form the pulverized synthetic quartz glass powder. The obtained high-viscosity synthetic quartz glass member contains 0.1-1,000ppm aluminum,  $\leq 10$ ppb each of metallic impurities other than Al and has  $\geq 1,225^{\circ}\text{C}$  annealing point,  $\geq 1,135^{\circ}\text{C}$  strain point and  $\leq 1$ ppm OH group and Cl concentrations.

COPYRIGHT: (C)1996,JPO

JP 08-040737

Machine Translation from JPO

**\* NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**NOTICES \***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

**DETAILED DESCRIPTION**

---

[Detailed Description of the Invention]

[0001]

[Industrial Application] the hyperviscous synthetic quartz glass with which this invention has the elevated-temperature viscosity more than a hyperviscous synthetic quartz glass member, especially a living-rock English electric-melting-of-glass article -- it is related with a member and its manufacture method

[0002]

[Description of the Prior Art] As the manufacture method of synthetic quartz glass. The silica particle which was made to understand silicon compounds, such as \*\* and 1 silicon tetrachloride, by flame adding water, and obtained them in the acid hydrogen flame is made to deposit on support. The method by the direct method which is made to carry out melting of this directly, and is used as quartz glass (refer to Japanese Patent Publication No. 3 No. -31010 official report), 2) A porous-glass base material is made for this silicon compound as ester silanes, such as methyl trimetoxysilane. The method by the soot method which fuses this and is used as quartz glass (refer to Japanese Patent Publication No. 4 No. -20853 official report), 3) Make the mixed gas of a silicon compound, oxygen, and a hydrogen chloride react in RF plasma flame, and a silicon dioxide is made to generate. The method by the plasma method make this deposit on support (refer to JP, 63-38343, B), 4) The method of being called the so-called sol-gel method which sinters the silica which understood alkoxysilane an added water part and obtained it under existence of an acid or an ammonia catalyst, and is used as quartz glass is learned.

[0003]

[Problem(s) to be Solved by the Invention] However, a hydroxyl-group content the quartz glass obtained by this direct method of 1 Since a chlorine content is -150ppm in 200-

1,000 ppm, there is a trouble of a low in elevated-temperature viscosity, and a hydroxyl-group content is [ a chlorine content ] -100ppm in -300ppm, and since chlorine contains even if it carries out chlorine dehydration, the quartz glass obtained by this soot method of 2 has the trouble that elevated-temperature viscosity does not become high. Moreover, although a hydroxyl-group content becomes free at the quartz glass obtained by this plasma method of 3, a chlorine content becomes high with -1,000ppm, and A production cost is high, and there is disadvantage that mass production is also difficult, and although a chlorine content becomes free, a hydroxyl-group content becomes the quartz glass obtained by this sol-gel method of 4 with -800ppm. Since it will become free [ a hydroxyl-group content ] if an ammonia catalyst is used, although an elevated-temperature viscosity article of the same grade as a living-rock English electric-melting-of-glass article can be obtained Since this has the long manufacturing process, it becomes cost quantity, in using an acid catalyst, a hydroxyl group remains, and since chlorine also remains in using a hydrochloric acid as an acid, the product of elevated-temperature viscosity has the fault of not being obtained.

[0004] on the other hand, about the manufacture method of this synthetic quartz glass How to add aluminum is also learned by this, and the dryness afterbaking join of the aluminium compound is added and carried out into the sol solution which mixes the solution which understands 1 alkyl silicate an added water part with the silica particle and acid reagent which understand an added water part with a basic reagent, and are obtained, and is obtained about this, and is obtained. How (refer to Provisional-Publication-No. 63 No. -123825 official report) to obtain transparent glass, 2) After making the tubular silica porosity object acquired by carrying out the rotation gelling of the sol solution which makes a silica particle a principal component diffuse aluminum alkoxide, Make the method and 3 methyl silicate which dry, sinter and are used as the base material for optical fibers understand an added water part under existence of ammonia, and it considers as a spherical silica particle. At this time, it is dehydrated and decarbonized and this is made to sinter, an alumina is doped, the obtained vitreous humour is refined the back according to trituration and screen, and, subsequently sintering, the method (refer to Japanese Patent Publication No. 5 No. -41565 official report) of carrying out the rarefaction and obtaining hyperviscous quartz glass, etc. are learned for the acid hydrogen flame.

[0005] In this case, it is thought that aluminum exists as an intermediate oxide for restoring the network structure divided with alkali metal (Na etc.) into quartz glass. Although the continuous network structure cannot be made from itself with [intermediate oxide Although it is thought that the hole between  $\text{SiO}_4$  tetrahedrons is occupied, the network structure is strengthened by] which shows the oxide which forms the continuous network structure under some conditions (physics of glass, Kyoritsu shuppan Co., Ltd. P18 reference), and operation of this aluminum, and elevated-temperature viscosity improves Since the above-mentioned 1 and the synthetic quartz glass obtained by the manufacture method of 2 have OH basis, its viscosity is low. It is not suitable for use to a heat-resistant member, and the distribution of aluminum with the uniform synthetic quartz glass obtained by the manufacture method of 3 is hard to be obtained, therefore there is a fault that nonuniformity is in viscosity.

[0006]

[Means for Solving the Problem] It is a thing about a member and its manufacture

method. the hyperviscous synthetic quartz glass with which this invention solved such disadvantage in a conventional method, and the fault -- This manufacture method the solution which carried out mixed churning of the aluminum alkoxide to a methyl silicate Understand without addition of alcohol an added water part under existence of ammonia, and an aluminum content silica particle is made. Dehydrate this, heat and are decarbonized, and fuse under a vacuum or reduced pressure and the obtained synthetic quartz glass ingot is ground. The back according to screen, magnetic separation and after refining and considering as a synthetic quartz glass powder, it is what fuses and is characterized by the bird clapper. this hyperviscous synthetic quartz glass member 1) aluminum concentration Metal impurities other than 0.1-1,000 ppm and aluminum (Fe, Na, K, calcium, Ti, Zn, Cr, Mn, Mg, Li, nickel, Cu) are all. By 10 or less ppb 2) A slowly cooling point A strain point above 1,225 degrees C It is 1,135 degrees C or more, and 3OH basis content is 1 ppm. Following and Cl concentration is 1 ppm. It is characterized by being the following.

[0007] namely, the hyperviscous synthetic quartz glass which this invention persons added aluminum and raised viscosity, as a result of examining many things that the new manufacture method of a member should be developed After adding and agitating an aluminum alkoxide first to the methyl silicate made about this well-known as first train material in a sol-gel method, The silica particle which understands an added water part under existence of ammonia, and contains aluminum is made. Apply to a well-known sol-gel method correspondingly below, and after being dehydrated and decarbonized, if this is refined the back according to pulverization and screen, it considers as a synthetic quartz glass powder and it fuses after fusing under a vacuum or reduced pressure and considering as a synthetic quartz glass ingot aluminum hyperviscous synthetic quartz glass since 0.1-1,000 ppm is contained, while finding out that a member is obtained Other metal impure amount of resources other than aluminum this thing It is 10 or less ppb and a slowly cooling point 1,225 degrees C or more and a strain point It becomes 1,135 degrees C or more, and each of OH basis contents and Cl concentration is 1 ppm. It checked becoming the following and this invention was completed. This is explained further in full detail below.

[0008]

[Function] this invention -- hyperviscous synthetic quartz glass -- the manufacture method of a silica sol [ in / a sol-gel method / about a member and its manufacturing method / in this manufacture method ] -- setting After adding and agitating an aluminum alkoxide to a methyl silicate, it understands an added water part under existence of ammonia. Although melting fabrication of this is carried out after making the silica particle containing aluminum, making a synthetic quartz glass ingot according to a well-known sol-gel method below, grinding this and considering as a synthetic quartz glass powder According to this, it is aluminum. Although 0.1-1,000 ppm is contained Content of other metal impurities It is 10 or less ppb and a slowly cooling point 1,225 degrees C or more and a strain point It becomes 1,135 degrees C or more, and OH basis content and Cl concentration are 1 ppm. The hyperviscous synthetic quartz glass member which is the following is obtained easily.

[0009] Although manufacture of the synthetic quartz glass by this invention is performed with a sol-gel method, an aluminum alkoxide is added and mixed by this invention by the methyl silicate as this first train agent. This aluminum alkoxide exists as a liquid in

ordinary temperature and an ordinary pressure, its adding-water decomposition temperature is comparatively low, and it is good that considering as what has a near methyl silicate and a near reaction rate specifically considers as aluminum Secang dolly butoxide [aluminum (sec-C<sub>4</sub>H<sub>9</sub>O)<sub>3</sub>] from a desirable thing.

[0010] Manufacture of this first train raw material trickles a suitable quantity of an aluminum alkoxide into a methyl silicate, and should just mix it uniformly with an agitator. It sets after vitrification and the rate of fixation of aluminum in the added aluminum alkoxide is a simultaneously. Since it is 100%, This addition is the amount of mixtures of this methyl silicate and aluminum butoxide, and an aluminum content (ppm) in synthetic quartz glass that what is necessary is just to set according to aluminum content of SiO<sub>2</sub> calculated on calculation. For example, it came to be shown in Table 1, and although the error of opposite *Perilla frutescens* (L.) Britton var. *crispa* (Thunb.) Decne. of the content of aluminum obtained is less than 5% at calculated value, let it be a desirable thing to carry out this mixture to dryness atmosphere in an airtight container on environment on work again.

[0011]

[Table 1]

始発原料中の重量		合成石英ガラス中の
メチルシリケート	Al (C <sub>4</sub> H <sub>9</sub> O) <sub>3</sub>	Al 含有量 (ppm)
10 kg	0.036 g	1.0
10 kg	1.798 g	50.0
10 kg	35.969 g	1000.0

[0012] Although the cohydrolysis of the mixed liquor of this methyl silicate and an aluminum alkoxide is carried out subsequently to the bottom of existence of ammonia, this introduces continuously this mixed liquor of 26.5l./o'clock, and 20% of the weight of 17.2l. [/o'clock] aqueous ammonia into the 5l. reactor made from Pyrex, and it should just make it agitate them with an agitator. this reaction formula -- following -- it is carried out by formula  $\text{Si}(\text{OCH}_3)_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{CH}_3\text{OH}$  and  $2\text{aluminum}(\text{C}_4\text{H}_9\text{O})_3 + 3\text{H}_2\text{O} \rightarrow \text{aluminum}_2\text{O}_3 + 6\text{C}_4\text{H}_9\text{OH}$ , and the silica which contains an aluminum oxide here generates

[0013] Thus, since the load [ as opposed to heating at the time of decarbonization in the lower one ] of the water content of the silica particle at this time decreases, it is [ that what is necessary is for a centrifugal separation machine or a press machine just to perform this dehydration ] desirable [ a water content ], although the obtained aluminum content silica particle is subsequently made into a synthetic quartz glass ingot by dehydration, decarbonization, and sintering to consider as 30 - 40% or less. Moreover, this decarbonization is this heating although it is necessary to heat in the atmosphere containing oxygen in order to oxidize a particle. It is preferably that what is necessary is just to consider as 800 to 1,200 degree C that oxidization cannot take place easily below 800 degrees C since weld between particles starts above 1,200 degrees C. It is good to consider as 1,000 to 1,100 degree C. In addition, since this promotes dryness and oxidization, it is good to carry out with rotary kiln.

[0014] In addition, this sintering is this heating although what is necessary is just to heat

at an elevated temperature under reduced pressure or a vacuum. What is necessary is not to fuse below 1,500 degrees C, and just to consider as 1,500 to 1,900 degree C above 1,900 degrees C, since sublimation becomes intense. Although what is necessary is just to change this heat treatment condition with the level of the synthetic quartz glass demanded, in order to obtain a thing without a content bubble, it sets under the high vacuum of 10 to 2 or more Torrs. It is good to heat at 1,700 to 1,900 degree C, and according to this, a transparent synthetic quartz glass ingot can be obtained.

[0015] thus -- since the manufactured synthetic quartz glass ingot subsequently refines this a trituration and screen exception -- this synthetic quartz powder -- melting -- fabricating -- synthetic quartz glass -- although what is necessary is just to define this screen exception by the use that what is necessary is for a jaw crusher, a hammer mill, a disc mill, a ball mill, etc. just to perform this trituration although considered as a member -- this -- for example, -- What is necessary is just to obtain the thing of about 200-350 micrometers. Moreover, although this refining may be excluded if it responds to a degree of contamination since it aims at removal of the contamination at the time of trituration, it should just perform rinsing, HF processing, HCl processing, magnetic separation, flotation, etc. to this.

[0016] In addition, this melting is Ar and N<sub>2</sub>. It is the bottom of the ordinary pressure in inert gas, such as gas, reduced pressure, and pressurization, or under [ air current ] setting. the same as the above 1,500 to 1,900 degree C -- desirable -- according to [ that what is necessary is just to carry out at 1,700 to 1,900 degree C ] this -- aluminum concentration 0.1-1,000 ppm -- metal impurities other than aluminum 10 or less ppb -- it is -- slowly cooling point 1,225 degrees C or more and strain point 1,135 degrees C or more -- it is -- OH basis concentration and Cl concentration -- each -- 1 ppm The hyperviscous synthetic quartz glass member which is the following can be obtained easily.

[0017]

[Example] the synthetic quartz glass in an example although the example of this invention and the example of comparison are given next -- the physical-properties value of a member shows the measured value by the following methods  
(Measurement of the amount of hydroxyl groups) It is OH absorption wavelength using IR (infrared radiation) measuring instrument and IR-Spectrophotometer TypeA -3 [the tradename made from Day Duty Light]. It estimates from 2.7-micrometer peak quantity.  
(Measurement of chlorinity) Made the neutron collide with a sample with a Rikkyo University reactor IRIGA-II type, the nuclear reaction was made to cause, the gamma ray was detected in the high grade germanium semiconductor detector and the multichannel pulse height analyzer, and Cl content was calculated.

[0018] (Measurement of a point [ distortion ] and a slowly cooling point) The heat characteristic of a point [ distortion ] and a slowly cooling point is typical, and they are the physical properties used as the index of elevated-temperature viscosity. Temperature in case viscosity is  $4 \times 10^{14}$  poise ( $\log \eta = 14.5$ ) shows a point [ distortion ], and a slowly cooling point shows temperature in case viscosity is 1013 poise ( $\log \eta = 13.0$ ). (Asakura Publishing Co., Ltd. "glass handbook" P 637 reference)

In the narrow temperature requirement, since the plot to the inverse number of the absolute temperature of  $\log \eta$  had a straight-line relation, it was extended in 1,100 degree C, 1,150 degree C, 1,200 degree C, 1,250 degree C, and 1,300 degree C, amount \*\*L was measured (Fiber-elongation method \*), and it asked for \*\*  $\eta$ . this -- vertical-

axis: -- it plotted to drawing of the inverse number of logeta and horizontal-axis: absolute temperature, and asked for the straight line It asked for the temperature which is distorted in the temperature equivalent to log eta=14.5 and is equivalent to a point and log eta=13.0 from this straight line as a slowly cooling point.

[0019] \* the Fiber-elongation method -- apply heat to a 4x2x40mm sample, ask for \*\*L (cm) of the sample in \*\*t= 120 - 3,000 seconds, and search for viscosity using the following formulas

$$\eta \text{ (ポイズ)} = \frac{980 \times W \text{ (g)} \times L \text{ (cm)} \times \Delta t \text{ (秒)}}{3 \times A \text{ (cm)} \times B \text{ (cm)} \times \Delta L \text{ (cm)}}$$

A= 0.4cm, B= 0.2cm, L= 4.0cm, the W=500 g \*\*t= measuring time (second), the amount of \*\*L= elongation (cm)

(Measurement of purity, and distribution measurement of aluminum) The fixed quantity of a trace element was performed using Hitachi MIP-MS elemental-analysis equipment (P-7000 type).

[0020] Example 1 methyl silicate It is aluminum sec-butoxide to 100kg. 18.0g was dropped, and it agitated for 5 minutes, and mixed, and this was made into the first train raw material of a reaction. Subsequently, it is 20% of the weight of aqueous ammonia to the 5l. reactor made from Pyrex. When put in 3l., the first train raw material of 26.5l./o'clock and 20% of the weight of the 17.2l. [/o'clock ] aqueous ammonia which were described above here are dropped continuously, the hydrolysis polycondensation was carried out at 40-50 degrees C, reaction mixture is created continuously and the filter press of this is carried out, particle size 200-700nm 40kg (15% of water contents) of spherical silica particles was obtained.

[0021] Since it was set to 34kg when it held for 1 hour and dehydration and decarbonization were carried out after carrying out a temperature up over 10 hours under existence of pure air by putting this silica particle into the container made from a quartz up to 1,000 degree C It is content volume about this. The carbon case of 3 (50cmx50cmx40cm) is stuffed 0.1m, and it is under the vacuum of 10-2Torr. When it sintered for 1 hour and took out from the furnace after the temperature fall at 1,800 degrees C, the exterior was transparent and with a height of 6cm synthetic quartz glass ingot 32kg was obtained on about 50cm square. After having ground this ingot by the conical ball mill (iron) next, making it 45 - 60# the screen exception and performing magnetic separation processing, it was immersed in 20% of HCl for 5 hours, and you made it immersed in 10% of HF for 10 minutes, and it rinsed, and considered as the synthetic quartz glass powder as refining processing. In addition, when the quartz crucible with a diameter of 18 inches was produced by arc rotation method about this synthetic quartz glass powder using this and the purity, viscosity, OH radical weight, and the amount of Cl(s) were measured about this piece of a crucible, the result as shown in Table 2 which carries out a postscript was obtained.

[0022] When set the addition of the aluminum sec-butoxide in an example 2 first-train raw material to 359.7g, and also the same processing as an example 1 was performed, the quartz crucible was produced and purity, viscosity, the amount of OH(s), and the amount of Cl(s) were measured about this piece of a crucible, the result as shown in Table 2 which carries out a postscript was obtained.

[0023] Addition of the aluminum sec-butoxide in an example 3 first-train raw material When it was referred to as 0.36g, and also the same processing as an example 1 was performed, the quartz crucible was produced and purity, viscosity, the amount of OH(s), and the amount of Cl(s) were measured about this piece of a crucible, the result as shown in Table 2 which carries out a postscript was obtained.

[0024] Example of comparison 1 methyl silicate When made this into the first train raw material for a reaction to 100kg, without aluminum sec-butoxide carrying out addition mixture, and also it processed like the example 1, the quartz crucible was produced and purity, viscosity, the amount of OH(s), and the amount of Cl(s) were measured about this piece of a crucible, the result as shown in Table 2 which carries out a postscript was obtained.

[0025]

[Table 2]

例No.		実施例 1	実施例 2	実施例 3	比較例 1	比較例 2
項目						
純 度	Al	50 ppm	1,000ppm	1 ppm	50 ppb	8 ppm
	Fe	8 ppb	7 ppb	8 ppb	7 ppb	275 ppb
	Na	2 ppb	3 ppb	1 ppb	2 ppb	111 ppb
	Ca	7 ppb	7 ppb	6 ppb	7 ppb	807 ppb
	K	<1 ppb	<1 ppb	<1 ppb	<1 ppb	122 ppb
	Ni	<1 ppb	<1 ppb	<1 ppb	<1 ppb	11 ppb
	Cu	<1 ppb	<1 ppb	<1 ppb	<1 ppb	17 ppb
	Cr	1 ppb	1 ppb	1 ppb	1 ppb	21 ppb
	Mn	1 ppb	1 ppb	1 ppb	1 ppb	122 ppb
	Mg	1 ppb	2 ppb	1 ppb	1 ppb	140 ppb
	Li	<1 ppb	<1 ppb	<1 ppb	<1 ppb	208 ppb
	Zn	2 ppb	2 ppb	2 ppb	2 ppb	84 ppb
	Ti	8 ppb	4 ppb	2 ppb	2 ppb	1,330 ppb
含有 O H 量		n. d.	n. d.	n. d.	n. d.	15 ppm
含有 C l 量		<1 ppm	<1 ppm	<1 ppm	<1 ppm	<1 ppm
粘性	歪み点	1,140℃	1,152℃	1,138℃	1,130℃	1,130℃
	徐冷点	1,235℃	1,259℃	1,230℃	1,228℃	1,220℃

[0026] 18" crucible was produced by the arc melting method using the example of comparison 2 electrical-and-electric-equipment melting living-rock English glass powder. About this piece of a crucible, when purity, viscosity, the amount of OH(s), and the amount of Cl(s) were measured, the result as shown in the next table 2 was obtained.

[0027]

[Effect of the Invention] According to the manufacture method of this invention, it is aluminum. Although 0.1-1,000 ppm is contained Other metal impure amount of resources It is 10 or less ppb and a slowly cooling point 1,225 degrees C or more and a strain point Above 1,135 degrees C, OH basis concentration and Cl concentration are 1 ppm. Since it is the following, the profitableness that the hyperviscous synthetic quartz glass member which is hyperviscosity in a high grade, therefore is made useful as a quartz crucible and



heat-resistant fixture material can be obtained easily is given.

---

[Translation done.]

#### NOTICES \*

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

#### CLAIMS

---

[Claim(s)]

[Claim 1] The solution which carried out mixed churning of the aluminum alkoxide to a methyl silicate Understand without addition of alcohol an added water part under existence of ammonia, and an aluminum content silica particle is made. the hyperviscous synthetic quartz glass which dehydrates this, heats, is decarbonized, fuses under a vacuum or reduced pressure, fuses the obtained synthetic quartz glass ingot after refining and considering as a synthetic quartz glass powder, after [ according to pulverization and screen ], magnetic separation, and, and is characterized by the bird clapper -- the manufacture method of a member

[Claim 2] 1) aluminum concentration Metal impurities other than 0.1-1,000 ppm and aluminum (Fe, Na, K, calcium, Ti, Zn, Cr, Mn, Mg, Li, nickel, Cu) are all. By 10 or less ppb 2) -- slowly cooling point 1,225 degrees C or more -- strain point 1,135 degrees C or more -- it is -- 3OH basis content -- 1 ppm following and Cl concentration -- 1 ppm the hyperviscous synthetic quartz glass manufactured by the manufacture method indicated by the claim 1 characterized by being the following -- member

---

[Translation done.]

